

Electrical Impedance Response of a Thick-Thin film Hybrid Anodic Nanoporous Alumina Sensor to Methanol Vapors.

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Abstract

The response of an anodic aluminum oxide (AAO) nanoporous humidity sensor to an organic vapor such as methanol is presented in this paper. Sensors constructed at Northern Illinois University were exposed to various organic vapors. The characteristic response of the sensor to various vapor dilutions was analyzed using real and complex impedance parameters.

Keywords: Nano-pores, hybrid thick film, sensors, methanol, AAO, Electrical Impedance Spectroscopy, Nyquist Plot, Cole-Cole Plot, Impedance

1 Introduction

Anodic anodized oxide (AAO) thin films for humidity sensing have been demonstrated by Dicky et al [1] and Haji-Sheikh et al [2]. Recent work to discover the sensitivity of AAO to other gases was performed by R. J. Lazarowich et al. [3] using a quartz microbalance. The main hypothesis in this work is to demonstrate that AAO sensors are not only sensitive to water condensation but also the condensation of higher vapor pressure liquids such as methanol and other organic species.

Researchers in Pennsylvania have demonstrated surface acoustic wave (SAW) devices made from self-ordered thin film porous alumina [4] for the sensing of ammonia and humidity. The AAO film used by Varghese et. al. [4] shows only local order and limited inter-domain alignment. The aluminum film used in this approach was produced using thermal evaporation and did not include a conductive adhesion layer. This experiment demonstrates the use of a conductive adhesion layer to produce a nanoporous sensor.

2 Experimental Procedure

To produce the thin-film nanopores, the starting substrate material is ninety-nine percent alumina. This substrate material was chosen for its low cost and ease of use. A

smoothing material was printed on the alumina to make the substrate compatible with thin film deposition. This smoothing layer process produces approximately 6000 nanometers (nm) of oxide. All processing was performed in a class-1000 clean room to minimize the effects of particles and impurities in the thick film material and the depositions took place in a Class 100 clean room. Initial experiments with thermally evaporated aluminum films on SiO₂ showed that an electrically conductive adhesion layer would be required to produce a robust anodically anodized oxide film on the substrate. This experiment showed that the film started to grow non-uniformly anodized nanopores that made the film problematic for use. The system chosen (shown in Figure 1) to produce the adhesion layer and the aluminum film is a production capable CVC, Inc deposition system (heretofore called the CVC system) with two DC magnetron targets and one RF target. The “glue” or adhesion layer selected was TiW due to its high affinity to both the aluminum film and SiO₂. This TiW layer is also very conductive (also with nanoscale grains) and will anodize in oxalic acid. The TiW layer was exposed to 3% (wt/wt) oxalic acid at 40 V for several hours in the initial experiments. This is similar to the case presented by Mukherjee et. al. [5] who anodized tungsten to form anodic nanoporous tungsten oxide in a tungsten film using oxalic acid. The film was then measured for resistivity with a 4-point probe and the resistance had changed little. This resistance measurement indicates that either the WO₃ is conductive or not very thick. The CVC was designed to deposit large wafer batches with a rotating anode. This rotation velocity can be varied. The rotation chosen allowed the substrates to be exposed to the plasma for three seconds at a time at 600W and 2 mTorr. This allows the system to build a film with multiple sub-monolayer depositions. The time calculated to produce a film of one micron of aluminum is 120 minutes and the time to produce the 0.1 μm of TiW glue layer is 20 minutes. To verify the thickness, the wafers were patterned using photolithography. This patterning creates a step in the aluminum that can facilitate thickness measurements. These measurements were made with an atomic force microscope (AFM). The Atomic force microscope used throughout this experiment is a Quesant Q-Scope 350 running in broadband wave mode.

The AFM scan of the as-deposited film is shown in Figure 2. The average grain size of this film is between 200 nm and 300 nm. This is important to note since the maximum number of pores that can fit in a single grain can be no more than 30 pores. This film does have a few large grains but these are not the majority. The large grains affect the reflectivity therefore creating a slight haze to the otherwise mirror like surface.



Figure 1. Sputter deposition system. This system is capable of depositing on substrates, which are as large as 6 inches. This system is cryo-pumped with a base pressure measured at 1.1×10^{-7} torr.

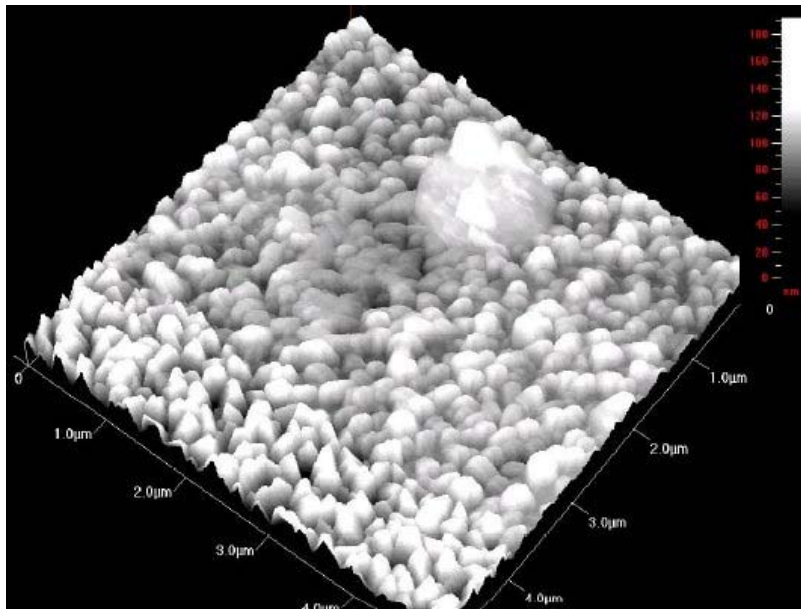


Figure 2. As-deposited nanocrystalline aluminum film. The average grain size is around 200 nm.

The film after anodization for thirty minutes at 25°C and 40 volts in a simple electrochemical cell has a slightly blue to green appearance. Since the substrate was connected at a point with a clip lead, there is a slight color gradient. Additionally, the metal thickness created an additional color gradient. The anodization setup is shown in Figure 3. The cathode in this setup is platinum while the anode is the silicon wafer coated in TiW/Al. The substrate was then rinsed for 15 minutes in deionized water then spin rinsed and spin dried. Using a four-point probe, this anodized film was determined to be non-conductive. To verify the porosity without using imaging, two clip leads were attached, one to the substrate and one to the film. The leads were then connected to a capacitance meter. The wafer was then exposed to water saturated air and if the wafer was properly anodized the capacitance would change by a factor of two. Figure 4 shows an AFM scan of the AAO film. Since the as-deposited film has a preferred orientation of [111] the pores are on the side of the “pyramidal” grains.



Figure 3. Simple electrochemical cell for anodizing thin films. The power supply produces 45V at 6A.

Thick-thin film hybrid AAO sensors were manufactured using alumina substrates. The surfaces of these substrates were specially prepared for the deposition of thin-film aluminum (1 micron) and the aluminum was then anodized in room temperature 4% oxalic acid. An

interdigitated capacitor was then patterned on the surface of the AAO using a screen printed conductor and fired on a belt furnace. This thick-thin film sensor had leads soldered on in a dual pin configuration that allows for easy handling and measurement.

3 Results

Organic vapors were created using a computer-controlled vapor generator. This device mixes a carrier gas (dry nitrogen) with saturated vapor, at 15C, to produce a prescribed dilution level. The impedance of the sensor, exposed to the various diluted samples, was measured using an Agilent 4980A LCR meter (Inductance-Capacitance-Resistance). The impedance model selected was the parallel resistor with a parallel capacitor. Figure 5 and Figure 6 show the results of measurements taken using the AAO based sensor when it was exposed to methanol and to water. The frequency range shown in this graph is 200 Hz to 200 kHz, though data was taken up to 2 MHz but didn't present any valuable data. .

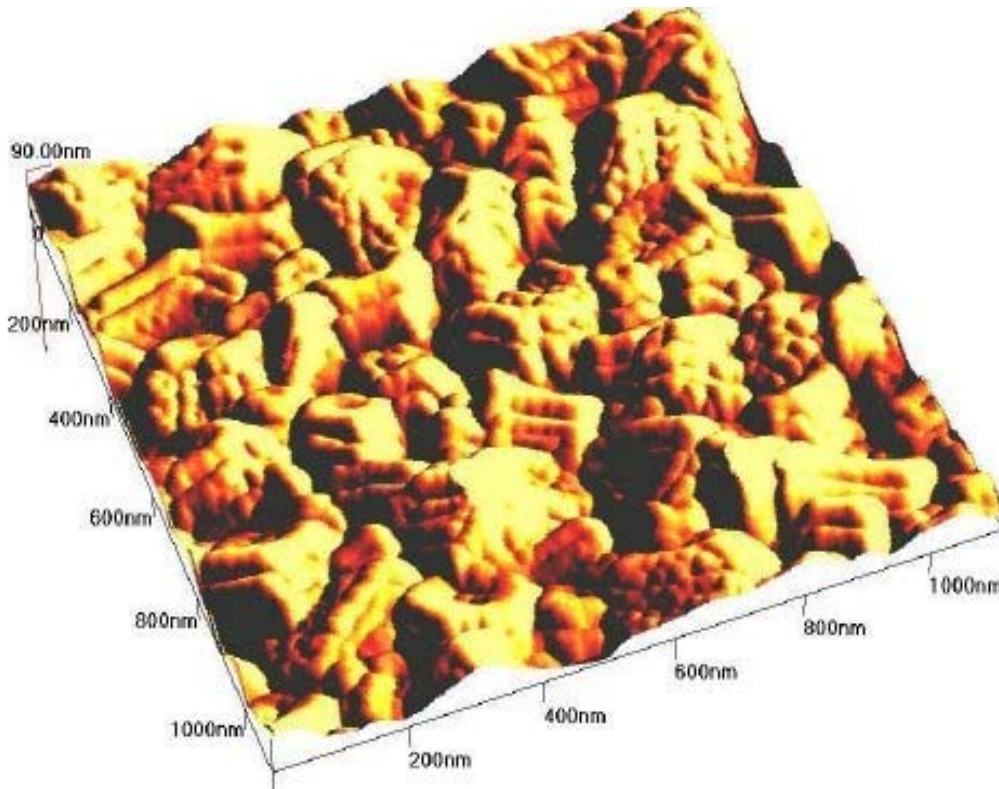
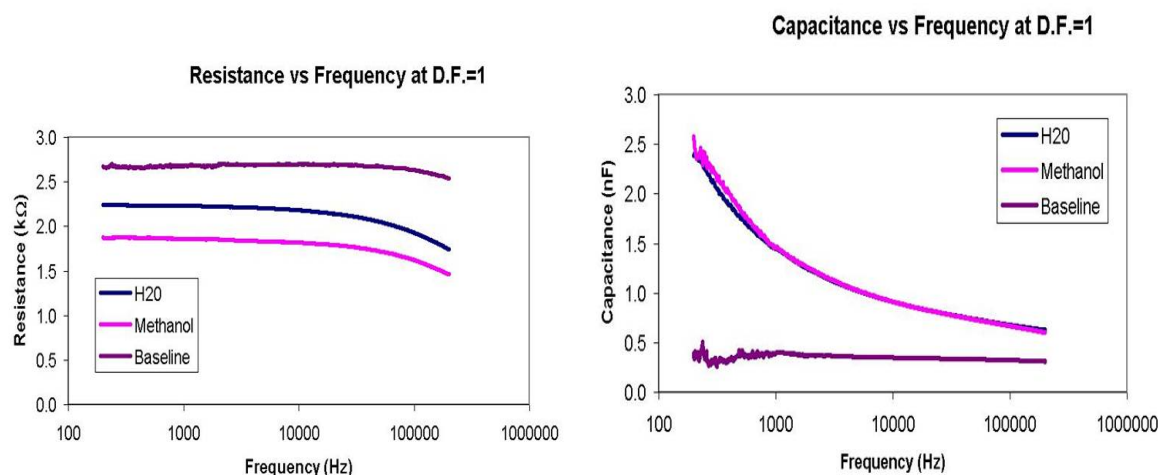


Figure 4. Atomic force microscopy of the AAO film. The average nanopore is around 40 nm in diameter and the original deposited aluminum grain size was 300 nm.

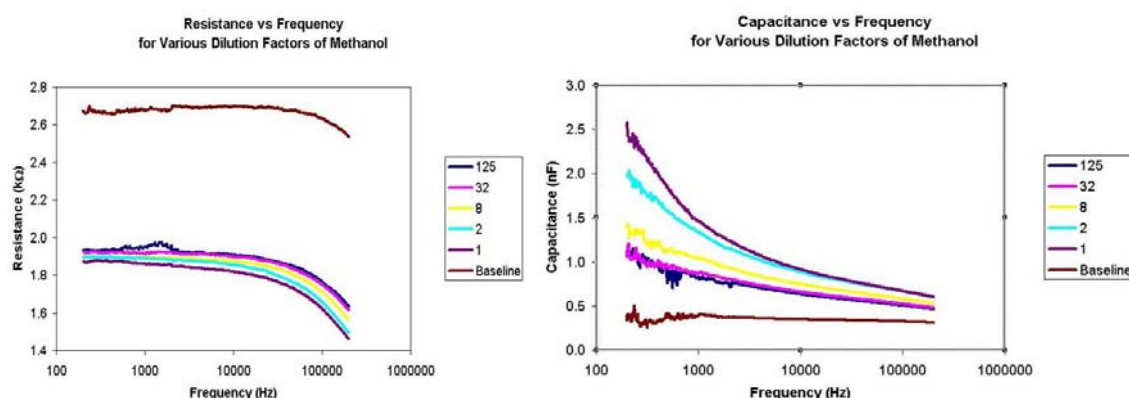


Figures 5 & 6. Comparison of thick-film hybrid AAO sensors with water and methanol vapors at the strongest vapor concentration. While capacitance is similar, the sensors resistance was different across the frequency range.

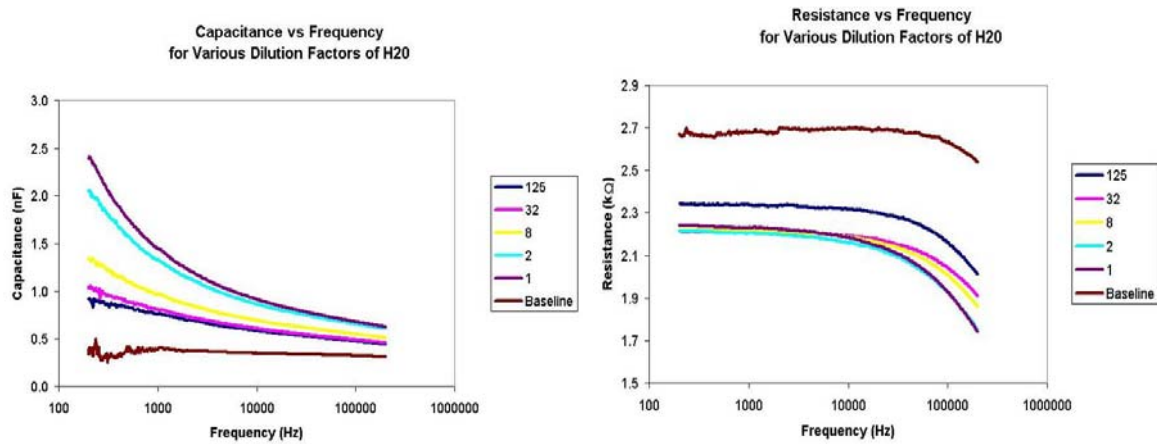
When the capacitance data are compared to dilution factor the data appear to be exponential and continues to stay sequential in order. The response is in the form

$$C_p = A \exp B / DF \quad (1),$$

where C_p is the parallel capacitance, A and B are coefficients of fit. The physical significance of these coefficients has not yet been investigated.

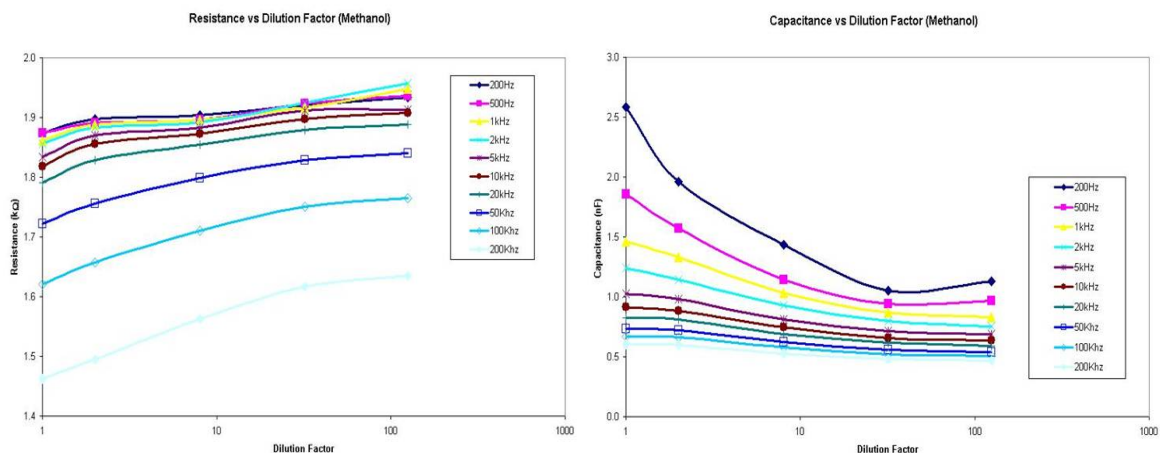


Figures 7 & 8. Capacitance and resistance versus frequency graphs for various dilutions of methanol

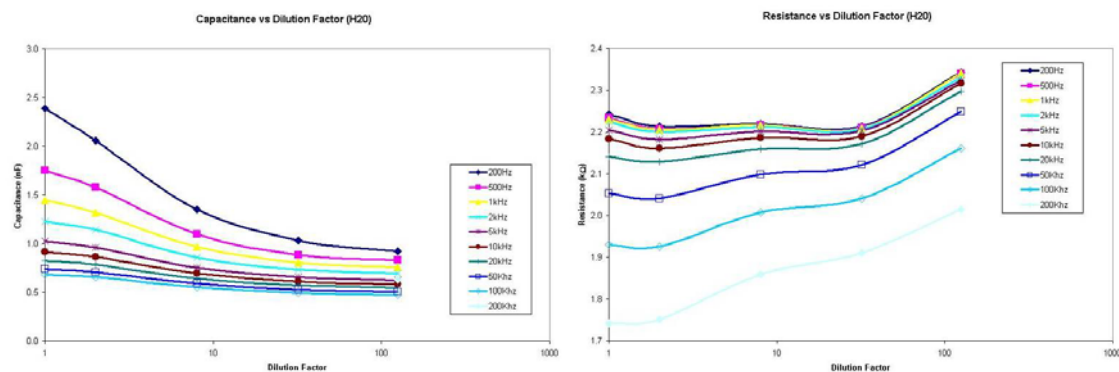


Figures 9 & 10. Capacitance and resistance versus frequency graphs for various dilutions of water

The exponential behavior is frequency dependent and concentration dependent with the highest sensitivity happening at the lowest frequencies. Figures 7-10 show the behavior of the sensor at different frequencies and different dilution factors for water and methanol. The response with varying frequency is significantly different than the response of methanol at various frequencies. Resistance varied at higher concentrations of methanol, especially at higher frequencies, however when sensing water the resistance was changed from baseline but didn't change among different concentrations.



Figures 11 & 12. Capacitance versus dilution factor for methanol.



Figures 13 & 14. Capacitance versus dilution factor for water.

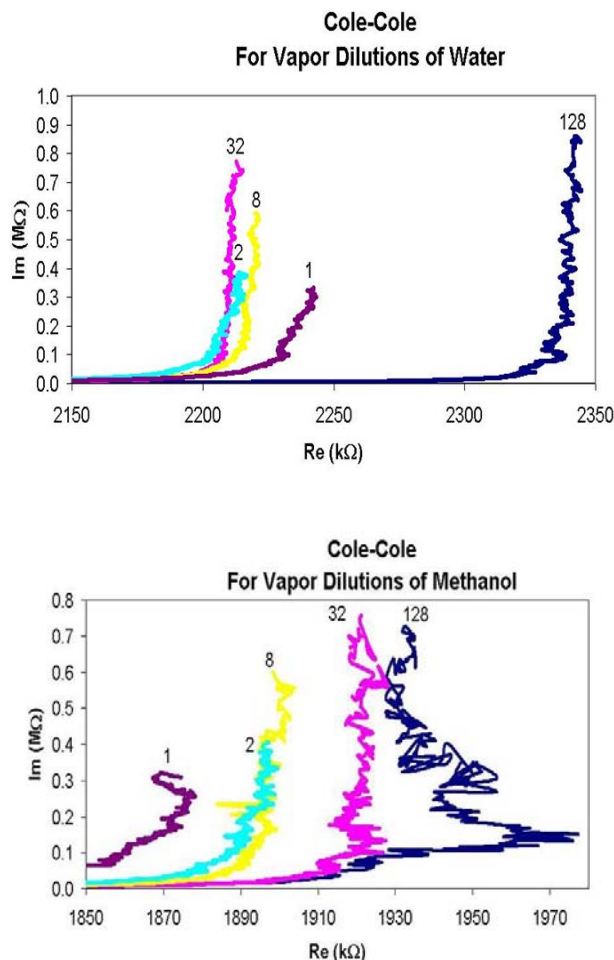
4 Impedance Spectroscopy

Electrical impedance spectroscopy (EIS) has been used as an analytical tool for several decades to determine the functional characteristics of surfaces with measurements performed in-situ. Conventional EIS analytical methods have typically employed a three-electrode system immersed in a buffered electrolyte and a frequency sweep is performed from DC to several kilohertz to determine the impedance characteristics of the analyte. The applications of EIS have been ubiquitous, however typical usage includes corrosion analysis and analysis of biomolecular binding to organic substrates.

The resultant EIS analysis generates a two-dimensional plot consisting of the real component (resistance) plotted along the abscissa and the imaginary component (impedance) along the ordinate. The nomenclature varies in the literature, however, these plots are commonly known as Nyquist or Cole-Cole plots [6]. In this experiment, true EIS measurements are not employed, however, the resultant complex impedance plots are generated using the capacitance and resistance data captured by an LCR meter. The observed impedance parameters varied as a function of the concentration of the analyte at the surface of the sensor.

The test configuration consists of the previously mentioned Agilent HP4980A LCR meter interfaced to a host-PC for real-time frequency sweep data collection and analysis. The LCR meter front end was interfaced to the sensor's interdigitated electrodes through the use of two low impedance null probes. Figures 15 and 16 denote the parametric shift of the sensor impedance as the analyte concentration is increased. The frequency sweep corresponds to the previously shown capacitance and resistance data (figures 11 - 14) of 200Hz to 2kHz with the

200Hz initial frequency appearing at the upper right-hand data point terminating with the 2kHz data point at the far left.



Figures 15 & 16. The Cole-Cole plots derived from the capacitance and resistance data. Note the orderly parametric shift in methanol as the dilution factor is decreased (increased MeOH concentration) at the sensor surface.

5 Conclusions

The AAO devices demonstrated in this paper show that the nanoporous material is sensitive to organic molecules. It also can be seen from the data in Figure 5 that methanol can be detected by using an AAO capacitive sensor. From this limited data set it appears that sensor has the ability to discriminate between water and methanol vapor. Future work will be performed to determine the sensor response to other organic vapors and the mechanism responsible for the interaction of the organic molecule with the AAO.

6 Acknowledgements

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7 References

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